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(54) Titre : MELANGE DE POLYMERES POSSEDANT UNE BONNE RESISTANCE AUX CHOCS A BASSE  
TEMPERATURE

(54) Title: POLYMER BLEND HAVING GOOD LOW-TEMPERATURE IMPACT STRENGTH

(57) Abrégé/Abstract:

A molding which comprises the following components: I. from 60 to 96.5% parts by weight of polyamide, II. from 3 to 39.5 parts by weight of an impact-modifying component which contains anhydride groups, III. from 0.5 to 20 parts by weight of a copolymer which contains units of the monomers a)  $\alpha$ -olefin, b) acrylic compound, and also c) olefinically unsaturated epoxide, carboxylic anhydride, carboximide, oxazoline or oxazinone, where the total of the parts by weight of components I, II and III is 100, and where moreover the polyamide has an excess of amino end groups, has improved low-temperature impact strength, even if the molding composition also comprises a plasticizer.

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Abstract:

A molding which comprises the following components:

- 5 I. from 60 to 96.5% parts by weight of polyamide,  
II. from 3 to 39.5 parts by weight of an impact-  
modifying component which contains anhydride  
groups,  
10 III. from 0.5 to 20 parts by weight of a copolymer  
which contains units of the monomers  
a)  $\alpha$ -olefin,  
b) acrylic compound, and also  
c) olefinically unsaturated epoxide, carboxylic  
15 anhydride, carboximide, oxazoline or oxazinone,

15 where the total of the parts by weight of components I,  
II and III is 100, and where moreover the polyamide has  
an excess of amino end groups, has improved low-  
temperature impact strength, even if the molding  
20 composition also comprises a plasticizer.

Polymer blend having good low-temperature impact strength

5 The invention relates to a material having good low-temperature impact strength and comprising, besides polyamide (PA) as matrix polymer, at least two other polymers which act synergistically to improve the impact strength of the material. The invention further relates to moldings made from this material.

10

Engineering components such as those used in the automotive industry sector, for example fuel lines which are tubes having one or more layers, nowadays have to fulfill very strict requirements with respect to low-temperature impact strength. To this end, tests are carried out using a variety of methods at a test temperature of -40°C, for example.

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It is known that when plasticizers are added to the polyamides frequently used for engineering components of this type, e.g. nylon-4,6, nylon-6,6, nylon-4,12, nylon-6,12, nylon-6, nylon-11 or nylon-12, the materials have poor low-temperature impact strength and it is therefore essential that these materials are modified appropriately.

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WO 95/22579 describes the impact-modification of polyamides using two impact modifiers, one modifier used being a modified EPM rubber or a modified EPDM rubber, while the other modifier used is a terpolymer made from ethylene and from an acrylic ester and glycidyl (meth)acrylate. This publication says nothing about the amino end group content of the polyamide. This is not surprising, since even if there is a considerable deficit of amino end groups, the bonding achieved between maleic-anhydride-functionalized EPM rubber or maleic-anhydride-functionalized EPDM rubber and polyamide is normally good.

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23443-733

- 2 -

The use of similar molding compositions as materials for layers in tubes having two or more layers has been described in EP-A-0 731 308, where again nothing is said about the amino end group content of the polyamide.

5           A major object of the invention is to provide molding compositions and moldings made therefrom having particularly high low-temperature impact strength. Another object is to provide molding compositions and moldings made therefrom having good low-temperature impact strength but with a lowest possible  
10 content of impact modifiers, so that there is a smallest possible effect on other important properties.

In this situation, the present invention provides a molding composition which comprises the following components:

- I.           from 60 to 96.5 parts by weight of polyamide,
- 15 II.          from 3 to 39.5 parts by weight of an impact-modifying component which contains an acid anhydride group, where the impact-modifying component is selected from the group consisting of ethylene/ $\alpha$ -olefin copolymers and styrene-ethylene/butylene block copolymers,
- 20 III.         from 0.5 to 20 parts by weight of a copolymer which contains units of the following monomers:
- a) from 20 to 94.5% by weight of one or more  $\alpha$ -olefins having from 2 to 12 carbon atoms,
- b) from 0 to 79.5% by weight of one or more acrylic  
25 compounds selected from the group consisting of:
- acrylic acid and methacrylic acid and salts thereof,

23443-733

- 3 -

- esters of acrylic acid and/or of methacrylic acid with a C<sub>1</sub>-C<sub>12</sub> alcohol, the esters optionally bearing a free hydroxyl or epoxide function,

- acrylonitrile and methacrylonitrile, and

5       - acrylamides and methacrylamides, and

c) from 0.5 to 80% by weight of an olefinically unsaturated epoxide, carboxylic anhydride, carboximide, oxazoline or oxazinone,

10       where the total of the parts by weight of components I, II and III is 100,

wherein the polyamide has more amino end groups than carboxyl end groups,

15       with the proviso (i) that the acrylic compounds (b) can be absent only when an epoxy group-containing ester of acrylic or methacrylic acid is employed as the monomer (c) and (ii) that the total of the monomers (b) and (c) is always at least 5.5% by weight.

In preferred embodiments, this molding composition comprises:

- 20   I.       from 65 to 90 parts by weight, particularly preferably from 70 to 85 parts by weight, of polyamide,
- II.       from 5 to 30 parts by weight, particularly preferably from 6 to 25 parts by weight, and preferably in particular from 7 to 20 parts by weight, of the impact-modifying component, and

23443-733

- 3a -

III. from 0.6 to 15 parts by weight, and particularly preferably from 0.7 to 10 parts by weight, of the copolymer, which preferably contains units of the following monomers:

- a) from 30 to 80% by weight of  $\alpha$ -olefin(s),
- 5        b) from 5 to 79.5%, more preferably from 7 to 70% by weight and particularly preferably from 10 to 60% by weight of the acrylic compound(s), and
- 10       c) from 0.5 to 50%, more preferably from 1 to 40% by weight, and particularly preferably from 5 to 30% by weight, of the olefinically unsaturated epoxide, carboxylic anhydride, carboximide, oxazoline or oxazinone.

Polyamides which may be used are mainly aliphatic homo- or copolycondensates, such as nylon-4,6, nylon-6,6, nylon-6,8, nylon-6,10, nylon-6,12, nylon-4,10, nylon-8,10, nylon-10,10, nylon-4,12, nylon-10,12, nylon-12,12, nylon-6, nylon-7, nylon-8, nylon-9, nylon-10, nylon-11 and nylon-12. (The naming of the polyamides corresponds to an international standard according to which the first numeral(s) give(s) the number of carbon atoms in the starting diamine, and the final numeral(s) give(s) the number of carbon atoms in the dicarboxylic acid. If only one numeral is mentioned, that means that the starting material was an  $\alpha,\omega$ -aminocarboxylic acid or the lactam derived therefrom. Reference may also be made to H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their properties], pp. 272 et seq. VDI-Verlag, 1976).

If use is made of copolyamides, these may contain adipic acid, sebacic acid, suberic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, for example, as coacid and, respectively, bis(4-aminocyclohexyl)methane, trimethylhexamethylenediamine, hexamethylenediamine or the like as codiamine. Lactams, such as caprolactam or laurolactam and, respectively, aminocarboxylic acids, such as  $\omega$ -aminoundecanoic acid, may likewise be incorporated as cocomponent.

The preparation of these polyamides is known (e.g. D.B. Jacobs, J. Zimmermann, Polymerization Processes, pp. 424-467, Interscience Publishers, New York, 1977; DE-B 21 52 194).

Other suitable polyamides are mixed aliphatic/aromatic polycondensates, as described in US Patents 2 071 250, 2 071 251, 2 130 523, 2 130 948, 2 241 322, 2 312 966, 2 512 606 and 3 393 210, and also in Kirk-Othmer,

Encyclopedia of Chemical Technology, 3rd edn., Vol. 18, pp. 328 et seq. and 435 et seq., Wiley & Sons, 1982.

5 Preferred suitable ethylene/ $\alpha$ -olefin copolymers of component II are:

- ethylene/ $C_3$ - $C_{12}$ - $\alpha$ -olefin copolymers containing from 20 to 96% by weight, preferably from 25 to 85% by weight, of ethylene. Examples of  $C_3$ - $C_{12}$ - $\alpha$ -olefins used are propene, 1-butene, 1-pentene, 1-hexene, 10 1-octene, 1-decene or 1-dodecene. Typical examples of these materials are ethylene-propylene rubber and also LLDPE and VLDPE.
- ethylene/ $C_3$ - $C_{12}$ - $\alpha$ -olefin/unconjugated-diene terpolymers containing from 20 to 96% by weight, 15 preferably from 25 to 85% by weight, of ethylene and up to at most about 10% by weight of an unconjugated diene, such as bicyclo[2.2.1]-heptadiene, 1,4-hexadiene, dicyclopentadiene or in particular 5-ethylidenenorbornene. Examples of 20 suitable  $C_3$ - $C_{12}$ - $\alpha$ -olefins are again propene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene or 1-dodecene.

25 The preparation of these copolymers or terpolymers with the aid of a Ziegler-Natta catalyst is prior art.

30 The styrene-ethylene/butene block copolymers preferably used are styrene-ethylene/butylene-styrene block copolymers (SEBS), which are obtainable by hydrogenating styrene-butadiene-styrene block copolymers. However, it is also possible to use diblock systems (SEB) or multiblock systems. Block copolymers of this type are prior art.

35 Component II contains anhydride groups which are introduced in a known manner by thermal or free-radical reaction of the main chain polymer with an unsaturated dicarboxylic anhydride, with an unsaturated



dicarboxylic acid, or with an unsaturated monoalkyl dicarboxylate, at a concentration sufficient for good bonding to the polyamide. Examples of suitable reagents are maleic acid, maleic anhydride, monobutyl maleate, fumaric acid, aconitic acid or itaconic anhydride. Using this method, it is preferable for from 0.1 to 4% by weight of an unsaturated anhydride to have been grafted onto impact-modifying component II. As in the prior art, it is also possible for another unsaturated monomer, such as styrene,  $\alpha$ -methylstyrene or indene, to be grafted on together with the unsaturated dicarboxylic anhydride or its precursor.

Examples of monomers used in the makeup of the copolymer of component III are as follows, this list not being comprehensive:

- a)  $\alpha$ -olefins, such as ethylene, propene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene or 1-dodecene, for example;
- b) acrylic acid, methacrylic acid or salts thereof, for example with  $\text{Na}^+$  or  $\text{Zn}^{2+}$  as counterion; methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, dodecyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl acrylate, 4-hydroxybutyl methacrylate, glycidyl acrylate, glycidyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-ethylacrylamide, N-hydroxyethylacrylamide, N-propylacrylamide, N-butylacrylamide, N-(2-ethylhexyl)acrylamide, methacrylamide, N-methylmethacrylamide, N,N-dimethylacrylamide, N-ethylmethacrylamide, N-hydroxyethylmethacrylamide, N-propylmethacrylamide, N-butylmethacrylamide,

23443-733

- 7 -

N,N-dibutylmethacrylamide, N-(2-ethylhexyl)methacrylamide;

c) vinyloxirane, allyloxirane, glycidyl acrylate, glycidyl methacrylate, maleic anhydride, aconitic anhydride, itaconic anhydride, and also the dicarboxylic acids arising  
5 from these anhydrides by reaction with water; maleimide, N-methylmaleimide, N-ethylmaleimide, N-butylmaleimide, N-phenylmaleimide, aconitimide, N-methylaconitimide, N-phenylaconitimide, itaconimide, N-methylitaconimide, N-phenylitaconimide, N-acryloylcaprolactam,  
10 N-methacryloylcaprolactam, N-acryloyllauro lactam, N-methacryloyllauro lactam, vinyloxazoline, isopropenyloxazoline, allyloxazoline, vinyloxazinone or isopropenyloxazinone.

If use is made of an epoxy group-containing ester of  
15 acrylic acid or methacrylic acid, such as glycidyl acrylate or of glycidyl methacrylate as the monomer c), it functions at the same time as the acrylic compound b), and therefore if the amount of the epoxy group-containing ester of (meth)acrylic acid is sufficient, there is no need for any other acrylic  
20 compound to be present. In this specific embodiment, the copolymer contains units of the following monomers:

a) from 20 to 94.5% by weight of one or more  $\alpha$ -olefins having from 2 to 12 carbon atoms,

b) from 0 to 79.5% by weight of one or more acrylic  
25 compounds, selected from the group consisting of

- acrylic acid and methacrylic acid and salts thereof,

- esters of acrylic acid and/or of methacrylic acid with a C<sub>1</sub>-C<sub>12</sub> alcohol,

23443-733

- 8 -

- acrylonitrile and methacrylonitrile,

- acrylamides and methacrylamides, and

c) from 0.5 to 80% by weight of an ester of acrylic acid or methacrylic acid, where the ester contains an epoxy  
5 group,

where the total of b) and c) is at least 5.5% by weight.

The copolymer of component III may contain a small amount of other copolymerized monomers, such as dimethyl  
10 maleate, dibutyl fumarate, diethyl itaconate or styrene, as long as these do not significantly adversely affect the properties.

The preparation of copolymers of this type is prior art. A wide variety of types is available commercially, for  
15 example as LOTADER<sup>®</sup> (Elf Atochem; ethylene/acrylate/tercomponent or ethylene/glycidyl methacrylate).

The polyamide of component I has an excess of amino end groups, the excess generally stemming from the use of a diamine as molecular-weight regulator during preparation of the  
20 polyamide. The excess of amino end groups may also be achieved by mixing a polyamide low in amino groups and a polyamide high in amino groups. The molar ratio of amino end groups to carboxyl end groups is to be at least 51:49, preferably at least 55:45, particularly preferably at least 60:40 and in  
25 particular preferably at least 70:30. The maximum value is not critical and may be the maximum technically achievable.

23443-733

- 8a -

Practically it may be about 95:5, more preferably 90:10.

In one advantageous embodiment, some of the polyamide of component I is in the form of polyamine-polyamide copolymer, specifically from 0.1 to 10 parts by weight, preferably from 5 0.2 to 5 parts by weight and particularly preferably from 0.25 to 3 parts by weight per 100 parts by weight of the polyamide.

The polyamine-polyamide copolymer is prepared using the following monomers:

O.Z. 5602

- 9 -

- a) from 0.5 to 25% by weight, preferably from 1 to 20% by weight, and particularly preferably from 1.5 to 16% by weight, based on the polyamine-polyamide copolymer, of a polyamine having at least 4 nitrogen atoms, preferably at least 8 nitrogen atoms, and particularly preferably at least 11 nitrogen atoms and a number-average molar mass  $M_n$  of at least 146 g/mol, preferably at least 500 g/mol, and particularly preferably at least 800 g/mol, and
- b) polyamide-forming monomers selected from the group consisting of lactams,  $\omega$ -aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid.

In one preferred embodiment, the amino group concentration in the polyamine-polyamide copolymer is in the range from 100 to 2500 mmol/kg.

Examples of classes of substances which may be used as polyamine are the following:

- polyvinylamines (Römpf Chemie Lexikon [Römpf's Chemical Encyclopedia], 9th edition, Vol. 6, p. 4921, Georg Thieme Verlag Stuttgart, 1992);
- polyamines which are prepared from alternating polyketones (DE-A 196 54 058);
- dendrimers, such as  
 $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N(CH_2)_2-N((CH_2)_2-N((CH_2)_3-NH_2)_2)_2$  (DE-A-196 54 179) or  
 tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N',N'-bis[2-[bis(2-aminoethyl)amino]ethyl]-1,2-ethanediamine,  
 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-[bis(2-aminoethyl)-

amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaaza-heptadecane-1,17-diamine (J.M. Warakowski, Chem. Mat. 1992, 4, 1000-1004);

- 5 - linear polyethyleneimines, which can be prepared by polymerizing 4,5-dihydro-1,3-oxazoles, followed by hydrolysis (Houben-Weyl, Methoden der Organischen Chemie [Methods in organic chemistry], Vol. E20, pp. 1482-1487, Georg Thieme Verlag  
10 Stuttgart, 1987);
- branched polyethyleneimines, which can be obtained by polymerizing aziridines (Houben-Weyl, Methoden der Organischen Chemie [Methods in organic  
15 chemistry], Vol. E20, pp. 1482-1487, Georg Thieme Verlag Stuttgart, 1987) and generally have the following distribution of amino groups:  
from 25 to 46% of primary amino groups,  
from 30 to 45% of secondary amino groups, and  
20 from 16 to 40% of tertiary amino groups.

In the preferred case, the polyamine has a number-average molar mass  $M_n$  of not more than 20 000 g/mol, particularly preferably not more than 10 000 g/mol, and  
25 in particular preferably not more than 5000 g/mol.

Lactams or  $\omega$ -aminocarboxylic acids which are used as polyamide-forming monomers contain from 4 to 19 carbon atoms, in particular from 6 to 12 carbon atoms. It is  
30 particularly preferable to use  $\epsilon$ -caprolactam,  $\epsilon$ -aminocaproic acid, caprylolactam,  $\omega$ -aminocaprylic acid, laurolactam,  $\omega$ -aminododecanoic acid and/or  $\omega$ -aminoundecanoic acid.

35 Examples of combinations of diamine and dicarboxylic acid are hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic

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acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. However, besides these it is also possible to use any  
5 other combinations, such as decamethylenediamine/dodecanedioic acid/terephthalic acid, hexamethylenediamine/adipic acid/terephthalic acid, hexamethylenediamine/adipic acid/caprolactam, decamethylenediamine/dodecanedioic acid/ $\omega$ -aminoundecanoic  
10 acid, decamethylenediamine/dodecanedioic acid/lauro-lactam, decamethylenediamine/terephthalic acid/lauro-lactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/lauro-lactam.

15 In one preferred embodiment, the polyamine-polyamide copolymer is prepared with the additional use of an oligocarboxylic acid which has been selected from the class consisting of from 0.015 to about 3 mol% of dicarboxylic acid and from 0.01 to about 1.2 mol% of  
20 tricarboxylic acid, based in each case on the total of the other polyamide-forming monomers. In the calculation of these proportions, when considering the combination of equivalents of diamine and dicarboxylic acid, each of these individual monomers is included. If  
25 use is made of a dicarboxylic acid, it is preferable to add from 0.03 to 2.2 mol%, particularly preferably from 0.05 to 1.5 mol%, very particularly preferably from 0.1 to 1 mol% and in particular from 0.15 to 0.65 mol%. If use is made of a tricarboxylic acid, it is preferable  
30 to use from 0.02 to 0.9 mol%, particularly preferably from 0.025 to 0.6 mol%, very particularly preferably from 0.03 to 0.4 mol%, and in particular from 0.04 to 0.25 mol%. The concomitant use of the oligocarboxylic acid markedly improves resistance to solvents and to  
35 fuels, in particular resistance to hydrolysis and alcoholysis.

The oligocarboxylic acid used may comprise any desired di- or tricarboxylic acid having from 6 to 24 carbon atoms, such as adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, isophthalic acid, 5 2,6-naphthalenedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, trimesic acid and/or trimellitic acid.

If desired, use may also be made of aliphatic, 10 alicyclic, aromatic, aralkyl and/or alkylaryl-substituted monocarboxylic acids having from 3 to 50 carbon atoms, e.g. lauric acid, unsaturated fatty acids, acrylic acid or benzoic acid, as regulator. Using these regulators can reduce the concentration of 15 amino groups without altering the structure of the molecule. This method can also be used to introduce functional groups, such as double bonds or triple bonds, etc. However, it is desirable for the polyamine-polyamide copolymer to have a substantial proportion of 20 amino groups. The amino group concentration in this copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly preferably in the range from 300 to 1100 mmol/kg. For the purposes of 25 the present invention, amino groups here and below are not only amino end groups but also any secondary or tertiary amine functions which may be present in the polyamine.

30 The polyamine-polyamide copolymers of the invention may be prepared by various processes.

One method consists in bringing the lactam and, respectively,  $\omega$ -aminocarboxylic acid and polyamine 35 together and then carrying out the polymerization or the polycondensation. The oligocarboxylic acid may be added either at the start or during the course of the reaction.



However, one preferred method is a two-stage process in which the lactam cleavage and prepolymerization is first carried out in the presence of water (as an  
5 alternative, the appropriate  $\omega$ -aminocarboxylic acids and, respectively, diamines and dicarboxylic acids are used directly and prepolymerized). In the second step, the polyamine is added, while any oligocarboxylic acid used concomitantly is metered in prior to, during or  
10 after the prepolymerization. The pressure is then released at temperatures between 200 and 290°C and polycondensation takes place in a stream of nitrogen or in vacuo.

15 Another preferred method consists in the hydrolytic degradation of a polyamide to give a prepolymer, and simultaneous or subsequent reaction with the polyamine. It is preferable to use polyamides in which the end-group difference is approximately zero, or in which any  
20 oligocarboxylic acid used concomitantly has previously been incorporated by polycondensation. However, the oligocarboxylic acid may also be added at the start of, or in the course of, the degradation reaction.

25 Using these methods it is possible to prepare ultra-high-branched polyamides with acid values below 40 mmol/kg, preferably below 20 mmol/kg and particularly preferably below 10 mmol/kg. Almost complete conversion is achieved after as little as from  
30 one to five hours of reaction time at temperatures of from 200 to 290°C.

If desired, a vacuum stage lasting a number of hours may follow, as another process step. This lasts for at  
35 least four hours, preferably for at least six hours, and particularly preferably for at least eight hours, at from 200 to 290°C. After an induction period of a number of hours, the melt viscosity is then observed to

increase, probably due to a reaction of amino end groups with one another, with elimination of ammonia and chain-linkage. This further increases the molar mass, and this is particularly advantageous for molding compositions intended for extrusion.

If there is a desire not to complete the reaction in the melt, solid-phase postcondensation of the polyamine-polyamide copolymer as in the prior art is also possible.

With the aid of the polyamine-polyamide copolymer, the ratio of amino end groups to carboxyl end groups in component I can be controlled. The result is a still further improvement in interaction between component I on the one hand and components II and III on the other, giving a still further improvement in low-temperature impact strength. At the same time, adding this copolymer also lowers the melt viscosity, and molding compositions of this type are therefore easier to process. This finding is surprising, since there is generally an inverse correlation between melt viscosity and impact strength.

Besides constituents I to III, the molding composition may also comprise relatively small amounts of additives which are needed to achieve certain properties. Examples of these are plasticizers, pigments or fillers, such as carbon black, titanium dioxide, zinc sulfide, silicates or carbonates, processing aids, such as waxes, zinc stearate or calcium stearate, flame retardants, such as magnesium hydroxide, aluminum hydroxide or melamine cyanurate, glass fibers, antioxidants, UV stabilizers, and also additives which give the product antistatic properties or electrical conductivity, e.g. carbon fibers, graphite fibrils, stainless steel fibers or conductivity black.

In one preferred embodiment, the molding composition comprises from 1 to 25% by weight of plasticizer, particularly preferably from 2 to 20% by weight, and in particular preferably from 3 to 15% by weight.

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Plasticizers and their use in polyamides are known. A general overview of plasticizers suitable for polyamides can be found in Gächter/Müller, Kunststoffadditive [Plastics additives], C. Hanser Verlag, 2nd edition, p. 296.

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Examples of the usual compounds suitable as plasticizers are esters of p-hydroxybenzoic acid having from 2 to 20 carbon atoms in the alcohol component, or amides of arylsulfonic acids having from 2 to 12 carbon atoms in the amine component, preferably amides of benzenesulfonic acid.

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Examples of plasticizers which may be used are ethyl p-hydroxybenzoate, octyl p-hydroxybenzoate, isohexadecyl p-hydroxybenzoate, N-n-octyltoluenesulfonamide, N-n-butylbenzenesulfonamide, or N-2-ethylhexylbenzenesulfonamide.

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The molding composition of the invention is used for producing moldings, e.g. for mechanical engineering, or for sports products, in particular for producing engineering components in the automotive industry sector. These are generally tubes, filler necks or containers, in particular for conducting or storing liquids or gases. A tube of this type may have a straight-line or corrugated shape, or may have corrugations only in some of its sections. Corrugated tubes are prior art (e.g. US 5 460 771) and further remarks concerning this topic are therefore unnecessary. Important applications are use as a fuel line, as a tank-filling pipe, as a vapor line (i.e. a line which conducts fuel vapors, e.g. a ventilation

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line), as a coolant-fluid line, as an air-conditioning-system line, or as a fuel tank. The molding composition is also advantageously used for quick connectors, pump housings, fuel-filter housings, activated-carbon  
5 canisters, valve housings, anti-surge cups, connectors to plastic fuel tanks, tank filler necks, cable coatings for electrical cables, housings for hydraulic cylinders, windshield-wash system lines, clutch lines, reduced-pressure lines, ventilation lines, hydraulic  
10 lines or air-brake lines.

The molding composition of the invention is also used for producing fuel-pump lines or for producing water-supply lines.

15 All of these moldings may either be composed entirely of the molding composition of the invention or may comprise the molding composition of the invention as one of two or more layers, for example as a reinforcing  
20 outer layer or as an inner layer, for example in a tube having two or more layers or container having two or more layers.

The moldings of the invention may be produced by a  
25 conventional prior art method, for example by extrusion, coextrusion, blow molding or injection molding.

#### Examples

30 The following materials were used in the experiments:

PA1: a commercially available nylon-6,12 with an excess of carboxyl end groups (acid value: 60 mmol/kg; amino end group concentration: 11 mmol/kg);  
35  $\eta_{rel} = 2.2$ ; VESTAMID® D22 from DEGUSSA-HÜLS AG

23443-733

- 17 -

PA2: a nylon 6,12 with an excess of amino end groups  
(acid value: 27 mmol/kg; amino end group  
concentration: 48 mmol/kg);  $\eta_{rel} = 2.2$

5 EXXELOR® VA 1803: a maleic-anhydride-grafted  
ethylene/propylene rubber as impact-  
modifying component (EXXON  
Chemicals)

10 LOTADER® AX 8900: a random terpolymer made from  
ethylene, about 32% by weight of  
acrylates and about 7-9% by weight  
of glycidyl methacrylate from  
ATOCHEM

15

BBSA: N-butylbenzenesulfonamide (plasticizer)

Comparative example 1:

100 parts by weight of PA1, 10 parts by weight of BBSA,  
20 10 parts by weight of EXXELOR® VA 1803 and 1 part by  
weight of LOTADER® AX 8900 were mixed in the melt,  
extruded and pelletized using a Berstorff ZE 25 33D  
twin-screw kneader, at 250°C and 200 rpm, with a  
throughput of 10 kg/h. The pellets were then used to  
25 produce extruded monotubes of dimensions 8 x 1 mm (i.e.  
8 mm external diameter and 1 mm wall thickness). The  
impact test results are given in table 1.

Example 1:

30 100 parts by weight of PA2, 10 parts by weight of BBSA,  
10 parts by weight of EXXELOR® VA 1803 and 1 part by  
weight of LOTADER® AX 8900 were mixed and further  
processed using a Berstorff ZE 25 33D twin-screw kneader  
as in comparative example 1. The impact test results  
35 are given in table 1.

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- 18 -

Comparative example 2:

As example 1, but without LOTADER® AX 8900; see table 1.

- 5 Table 1: Impact strength at -40°C, measured on tubes of dimensions 8 × 1 mm

Standard	Fracture ratio: number of fractures per 10 tubes tested		
	Comparative example 1	Example 1	Comparative example 2
SAE J844 (impact weight 455 g)	2	0	1
SAE J 2260 (impact weight 912 g)	0	0	0
VW/Audi (impact weight 500 g)	5	0	6
DIN 73378	0	0	0

23443-733

- 19 -

CLAIMS:

1. A molding composition which comprises the following components:

(I) from 60 to 96.5 parts by weight of polyamide,

5 (II) from 3 to 39.5 parts by weight of an impact-modifying component which contains an acid anhydride group, where the impact-modifying component is selected from the group consisting of ethylene/ $\alpha$ -olefin copolymers and styrene-ethylene/butylene block copolymers, and

10 (III) from 0.5 to 20 parts by weight of a copolymer which contains units of the following monomers:

a) from 20 to 94.5% by weight of one or more  $\alpha$ -olefins having from 2 to 12 carbon atoms,

15 b) from 0 to 79.5% by weight of one or more acrylic compounds selected from the group consisting of (i) acrylic acid, methacrylic acid or salts thereof, (ii) esters of acrylic acid or methacrylic acid with a  $C_1$ - $C_{12}$  alcohol, (iii) acrylonitrile or methacrylonitrile and (iv) acrylamides or methacrylamides, and

20 c) from 0.5 to 80% by weight of an olefinically unsaturated epoxide, carboxylic anhydride, carboximide, oxazoline or oxazinone,

where the total of the parts by weight of components (I), (II) and (III) is 100, and

25 wherein the polyamide (I) has more amino end groups than carboxyl end groups,

23443-733

- 20 -

with the proviso (i) that the acrylic compounds (b) can be absent only when an epoxy group-containing ester of acrylic or methacrylic acid is employed as the monomer (c) and (ii) that the total of the monomers (b) and (c) is always at least 5.5% by weight.

2. The molding composition as claimed in claim 1, wherein the impact-modifying component (II) has 0.1 to 4% by weight of an unsaturated dicarboxylic anhydride grafted to the ethylene/ $\alpha$ -olefin copolymer or the styrene-ethylene/butadiene block copolymer.

3. The molding composition as claimed in claim 1 or 2, wherein the ethylene/ $\alpha$ -olefin copolymer used as a base of the impact-modifying component (II) is (1) an ethylene/ $C_3$ - $C_{12}$ - $\alpha$ -olefin copolymer rubber having an ethylene content of 20 to 96% by weight or (2) an ethylene/ $C_3$ - $C_{12}$ - $\alpha$ -olefin/unconjugated diene terpolymer rubber having an ethylene content of 20 to 96% by weight and an unconjugated diene content of up to 10% by weight.

4. The molding composition as claimed in claim 1 or 2, wherein the styrene-ethylene/butylene block copolymer used as a base of the impact-modifying component (II) is a styrene-ethylene/butylene-styrene block copolymer (SEBS).

5. The molding composition as claimed in any one of claims 1 to 4, wherein the copolymer (III) is made of the following monomers:

- (a) from 20 to 94.5% by weight of the  $\alpha$ -olefin;
- (b) from 5 to 79.5% by weight of the acrylic compound; and



23443-733

- 21 -

(c) from 0.5 to 50% by weight of the olefinically unsaturated epoxide, carboxylic anhydride, carboxamide, oxazoline or oxazinone.

6. The molding composition as claimed in claim 5,  
5 wherein the monomer (c) of the copolymer (III) is selected from the group consisting of vinyloxirane, allyloxirane, maleic anhydride, aconitic anhydride, itaconic anhydride, maleic acid, aconitic acid, itaconic acid, maleimide, N-methylmaleimide, N-ethylmaleimide, N-butylmaleimide, N-phenylmaleimide,  
10 aconitimide, N-methyлаconitimide, N-phenylaconitimide, itaconimide, N-methylitaconimide, N-phenylitaconimide, N-acryloylcaprolactam, N-methacryloylcaprolactam, N-acryloyllauro lactam, N-methacryloyllauro lactam, vinyloxazoline, isopropenyloxazoline, allyloxazoline,  
15 vinyloxazinone and isopropenyloxazinone.

7. The molding composition as claimed in any one of claims 1 to 4, wherein the copolymer (III) has the following makeup:

(a) from 20 to 94.5% by weight of one or more  $\alpha$ -  
20 olefins having from 2 to 12 carbon atoms,

(b) from 0 to 79.5% by weight of one or more acrylic compounds selected from the group consisting of (i) acrylic acid, methacrylic acid or salts thereof, (ii) esters of acrylic acid or methacrylic acid with a C<sub>1</sub>-C<sub>12</sub> alcohol, (iii)  
25 acrylonitrile or methacrylonitrile and (iv) acrylamides or methacrylamides, and

(c) from 0.5 to 80% by weight of an ester of acrylic acid or methacrylic acid, where the ester contains an epoxy group,

23443-733

- 22 -

where the total of (b) and (c) is at least 5.5% by weight.

8. The molding composition as claimed in claim 7, wherein the acrylic compound (b) is absent in the copolymer (III).

9. The molding composition as claimed in any one of claims 1 to 8, wherein the acrylic compound (b) of the copolymer (III) is a member selected from the group consisting of acrylic acid, methacrylic acid, Na or Zn salt of acrylic or methacrylic acid, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, dodecyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl acrylate, 4-hydroxybutyl methacrylate, glycidyl acrylate, glycidyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-ethylacrylamide, N-hydroxyethylacrylamide, N-propylacrylamide, N-butylacrylamide, N-(2-ethylhexyl)acrylamide, methacrylamide, N-methylmethacrylamide, N,N-dimethylacrylamide, N-ethylmethacrylamide, N-hydroxyethylmethacrylamide, N-propylmethacrylamide, N-butylmethacrylamide, N,N-dibutylmethacrylamide, and N-(2-ethylhexyl)methacrylamide.

10. The molding composition as claimed in any one of claims 1 to 9, wherein the  $\alpha$ -olefin (a) of the copolymer (III) is ethylene.

11. The molding composition as claimed in claim 5, wherein in the copolymer (III), the  $\alpha$ -olefin (a) is ethylene,

23443-733

- 23 -

the acrylic compound (b) is a C<sub>1</sub>-C<sub>12</sub> alcohol ester of acrylic or methacrylic acid and the monomer (c) is glycidyl acrylate or methacrylate.

12. The mold composition as claimed in claim 8, wherein  
5 the copolymer (III) is ethylene/glycidyl methacrylate.

13. The molding composition as claimed in any one of  
claims 1 to 12, wherein the polyamide (I) is a member selected  
from the group consisting of nylon-4,6, nylon-6,6, nylon-6,8,  
nylon-6,10, nylon-6,12, nylon-4,10, nylon-8,10, nylon-10,10,  
10 nylon-4,12, nylon-10,12 and nylon-12,12.

14. The molding composition as claimed in any one of  
claims 1 to 12, wherein the polyamide (I) is a member selected  
from the group consisting of nylon-6, nylon-7, nylon-8, nylon-  
9, nylon-10, nylon-11, and nylon-12.

15 15. The molding composition as claimed in any one of  
claims 1 to 14, wherein in component (I), from 0.1 to 10 parts  
by weight per 100 parts by weight of the polyamide are in the  
form of polyamine-polyamide copolymer which has been prepared  
using the following monomers:

20 a) from 0.5 to 25% by weight, based on the polyamine-  
polyamide copolymer, of a polyamine having at least 4 nitrogen  
atoms and a number-average molar weight  $M_n$  of at least 146  
g/mol, and

b) polyamide-forming monomers selected from the group  
25 consisting of lactams,  $\omega$ -aminocarboxylic acids and equimolar  
combinations of diamine and dicarboxylic acid.

16. The molding composition as claimed in any one of  
claims 1 to 15, wherein the polyamide (I) has a molar ratio of

23443-733

- 24 -

the amino end groups to the carboxyl end groups of at least 60:40.

17. The molding composition as claimed in any one of claims 1 to 16, which further contains from 1 to 25% by weight  
5 (based on the molding composition) of a plasticizer.

18. The molding composition as claimed in any one of claims 1 to 16, which has been rendered antistatic or electrically conductive.

19. A molding produced from the molding composition as  
10 claimed in any one of claims 1 to 18.

20. The molding as claimed in claim 19, which is an engineering component in an automotive industry sector.

21. The molding as claimed in claim 19 or 20, which is a tube, a filler neck or a container.

15 22. A molding as claimed in claim 19 or 20, which is a fuel line, a tank-filling pipe, a vapor line, a fuel-pump line, a coolant-liquid line, an air-conditioning-system line, a fuel container, a quick connector, a pump housing, a fuel-filter housing, an activated-carbon canister, a valve housing, an  
20 anti-surge cup, a connector to a plastic fuel tank, a tank filler neck, a cable coating for an electrical cable, a housing for a hydraulic cylinder, a windshield-wash-system line, a clutch line, a reduced-pressure line, a ventilation line, a hydraulic line, an air-brake line or a water-supply line.

25 23. The molding as claimed in any one of claims 19 to 22, which is one of two or more layers.

24. The molding as claimed in claim 23, which is a tube having two or more layers.

23443-733

- 25 -

25. The molding as claimed in any one of claims 19 to 24, produced by extrusion, coextrusion, blow molding or injection molding.

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